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LETTERS  
TO THE EDITOR

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*Dedicated to V. F. Mironov on His 60th Anniversary*

## Synthesis and Structure of *N,N'*-Bis(dihexylphosphorylmethyl)-1,4-diaminobutane

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**Abstract**—*N,N'*-Bis(dihexylphosphorylmethyl)-1,4-diaminobutane has been obtained via the Kabachnik–Fields reaction. Crystal structure of its salt with nitric acid (bisphosphoryldiammonium dinitrate) has been studied.

**Keywords:** diphosphoryldiamine, aminophosphoryl extracting agent, complex, molecular structure

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We have earlier demonstrated high efficiency and selectivity of liquid and membrane extraction of organic and inorganic substrates (alkali, alkaline-earth, and rare metal ions as well as inorganic and organic acids) using phosphorylated diamines and azapodands as extracting agents [1–3]. We have also found that *N,N'*-bis(dialkylphosphorylmethyl)diaminoalkanes exhibit high selectivity with respect to nitric acid during the membrane extraction of inorganic acids: its transport was two orders of magnitude faster in comparison with phosphoric acid, whereas sulfuric acid has not been transported at all under the experiment conditions [4]. It should be noted that industrial extraction of metals from ore raw material is based on the use of aqueous solutions of the metal salts in the presence of strong inorganic acids (most often nitric acid). Hence, elucidation of structure of the transported complexes with acidic species involved in the membrane extraction is essential for understanding the mechanism of the carrier extracting action and the process optimization. X-ray structure analysis of the transported complexes of aminophosphoryl extracting agents with a substrate has not been reported so far. We have just recently discussed the crystal structure of *N*-(diphenylphosphorylmethyl)-*N*-methylaminoacetic acid complexes with copper(II) and nickel(II) ions; such data reflect

the coordination of the complexes formed between this aminophosphoryl carrier and doubly-charged metal ions during the extraction process [5].

In this study we report the crystal structure of *N,N'*-bis(dihexylphosphorylmethyl)-1,4-diaminobutane salt with nitric acid. We have earlier found that nitrogen atom is the most probable site of aminophosphoryl species protonation with acidic substrates, even though the participation of phosphoryl oxygen atom(s) in the formation of the carried complex cannot be ruled out as well. Moreover, intramolecular hydrogen bond can be formed in the molecules of  $\alpha$ -aminoalkylphosphoryl compounds containing secondary nitrogen atom in the P(O)CR<sub>2</sub>NH part, as shown in Scheme 1 for complex **A** [6]. The available experimental data have suggested that the carried complex can be of the 1 : 1 composition with intra- and intermolecular hydrogen bonds of type **A** or with chelate structure **B** described in detail in [1]. Bisphosphoryldiammonium dinitrate was likely formed at the diamine: acid ratio 1 : 2 as a result of protonation of both nitrogen atoms.

Using the Kabachnik–Fields reaction in the three-component dihexylphosphinite–paraformaldehyde–1,4-diaminobutane system in toluene with *p*-toluenesulfonic acid as the catalyst we synthesized *N,N'*-bis(dihexyl-